42



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# RELATION OF CLAY MINERALOGY TO ORIGIN AND RECOVERY OF PETROLEUM

BY
RALPH E. GRIM

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# RELATION OF CLAY MINERALOGY TO ORIGIN AND RECOVERY OF PETROLEUM[1]

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## ABSTRACT

The clay-mineral concept of the nature of clays and shales is briefly discussed in its relation to problems of the origin and recovery of oil and gas.

The character of the clay minerals that make up a sediment is to a considerable degree the result of diagenetic changes in the environment of accumulation. Diagenetic changes suggested by present available data are considered.

The relation of various clay minerals to organic material in argillaceous sediments is discussed in the light of evidence which suggests that certain clay minerals under certain conditions are the key factor in the transition of organic matter to petroleum.

The properties of clay minerals are considered as a basis for analyzing the effect of water with dissolved electrolytes, moving through a sand, on any clay in the sand. The characteristics of the clay minerals are believed to be significant factors in the recovery of oil.

Other significant effects of the properties of the various clay minerals are discussed.

## INTRODUCTION

Extensive researches in recent years have shown that clay materials, including shales, are composed essentially of extremely small crystalline particles of members of any one or more of a few groups of minerals known as the "clay minerals" (4).[3] In addition to the clay minerals, variable but usually small amounts of quartz, calcite, limonitic material, organic material, feldspar, and a host of other minerals may be present as extremely minor constituents, or as prominent constituents in occasional clays. Amorphous material has been proved in only a very few of the great number of soils, clays and shales that have been studied, and it is clear that it is not a significant factor in clays generally.

The factors which are necessary to characterize completely a clay material and also those that control its properties may be listed as follows.

1. Clay-mineral composition—the relative abundance of the clay-mineral components and their particle-size distribution.
2. Non-clay-mineral composition—the relative abundance of each mineral and the size-grade distribution of its particles.
3. Electrolyte content—the kind and amount of the exchangeable ions and any water-soluble salts.
4. Organic content—the amount, kind, and relation to other components.
5. Miscellaneous textural characteristics such as shape of quartz grains, degree of parallel orientation of the clay-mineral particles, and silicification.

The clay minerals are the essential constituents of clay materials and they are the most important single factor in determining the properties of these materials. There are three general kinds of clay minerals: (1) minerals in which the individual ultimate units have a sheet or flake shape; (2) minerals in which the ultimate

[1] Read before the Association at Los Angeles, March 27, 1947. Manuscript received, May 9, 1947.

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[3] Numbered references are listed at the end of this article. Reference 4 contains an extensive bibliography on the structure, properties, occurrence, and methods of study of the clay minerals.

units are fibrous or lath-shaped; and (3) amorphous minerals. The sheet or flake-shaped clay minerals are by far the most abundant, and the best known. The amorphous components have been proved in only a few clays. The more common and well known clay minerals are listed in Table I.

Researches in many fields (mineralogy, geology, chemistry, engineering, agriculture) have led to fairly adequate methods of identifying the clay minerals and have provided considerable information on their structure, composition, properties, and occurrence. The analytical methods and clay mineralogical data are covered in a voluminous literature (4) which is not reviewed herein. Many of these clay mineralogical data are very important in problems of the origin, recovery, and refining of petroleum. Of particular significance is the work that has

TABLE I

CLAY MINERALS

| | *Composition* |
|---|---|
| 1. Kaolinite group | |
| a. Equidimensional flake-shaped units | |
| Kaolinite | $(OH)_8Al_4Si_4O_{10}$ |
| Anauxite | |
| b. Lath-shaped units | |
| Halloysite minerals | $(OH)_8Al_4Si_4O_{10}$ <br> $(OH)_8Al_4Si_4O_{10} \cdot 4H_2O$ |
| 2. Montmorillonite group | |
| a. Equidimensional flake-shaped units | |
| Montmorillonite | $(OH)_4(Al_4 \cdot Fe_4 \cdot Mg_4)Si_8O_{20} \cdot nH_2O$ |
| b. Lath- or needle-shaped units | |
| Nontronite | |
| Hectorite | $(OH)_4(Mg \cdot Li)_6Si_8O_{20}$ |
| 3. Illite group | $(OH)_4K_y(Al_4 \cdot Fe_4 \cdot Mg_4)(Si_{8-y} \cdot Al_y)O_{20}$ |
| Insufficient data to subdivide | |
| 4. Miscellaneous fiber-shaped units | |
| Attapulgite | $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ |
| Sepiolite-like | $(OH)_4Mg_6Si_8O_{20} \cdot ?H_2O$ |
| 5. Amorphous | |

been done on the structure of the clay minerals, which has greatly increased our understanding of the fundamental causes of their properties and the factors that determine their origin. It is proposed, herein, to analyze some of these clay-mineral data in relation to such problems, and to indicate researches on the subject that appear desirable and promising.

## CLAY MINERALS AS CLUES TO ENVIRONMENT OF ACCUMULATION OF ARGILLACEOUS SEDIMENTS

It has long been the idea of many geologists that clay is an end-product of weathering and a material of great stability. As a generality this is simply not true. On the contrary, clay minerals are dynamic things, and great and important changes in structure, composition, and properties may result when a change takes place in the parameters of the environment in which the clay mineral is

found. The material is an end-product only so long as there is no environmental change. A clay-mineral composition that would be in equilibrium with one environment would probably not be in equilibrium with another environment. For example, kaolinite is a product of weathering in some areas, but it is certainly not the weathering product in all areas.

Clay minerals may change quickly, commonly in a matter of years, in response to changes in environment. Investigators of soils have proved the dynamic character of the clay minerals beyond reasonable doubt, and only one bit of evidence need be mentioned. Careful detailed studies have shown that illite develops from other clay minerals in a matter of years as a consequence of the addition of potash fertilizer in some soils and under certain conditions (12).

Since clay minerals are dynamic things, one would suspect that they might undergo important diagenetic changes. Few specific data on actual diagenetic changes in argillaceous sediments are available, but what evidence (2, 5) there is points to the conclusion that the clay-mineral composition of sediments is largely a result of conditions in the environment of accumulation, such as alkalinity of water, character of dissolved salts, temperature, rate of accumulation, and kind and amount of organic material. Furthermore, the evidence indicates that the diagenetic changes take place rapidly—a major part probably takes place quickly after the sediment arrives in the environment of accumulation. The character of the source material is important, for one would suspect on the basis of the structure of the clay minerals that kaolinite would be relatively resistant to change, whereas montmorillonite and illite would be less resistant, and perhaps the fibrous clay minerals would be least resistant of all. It is interesting that montmorillonite is a common product of present-day weathering under certain conditions, but rare in ancient marine sediments. It is suggestive that illite is the dominant clay-mineral component of many marine argillaceous sediments. Illite is the clay mineral in many, perhaps most, marine shales—its origin is probably due largely to diagenetic processes. In general the changes should be greater in a marine or brackish-water environment than in one with fresh water.

Considerable work has been done on the synthesis (9) of the clay minerals in the laboratory, and soil investigators (8) are studying the kind of clay minerals that are developing under certain weathering conditions. As yet the results do not permit any broad generalizations, but they do show that the presence of certain chemical elements in certain amounts greatly aids (or is required at times for) formation of certain clay minerals. Thus, potash is necessary for illite to form, and magnesium seems to be essential for at least some montmorillonite.

As the character of the clay mineral is a consequence of the environment, it should be possible to interpret the environment from clay-mineral data. This does not mean that simple determinations of the presence of illite or montmorillonite-type mineral will be adequate. Rather it is going to be necessary to determine the kind of montmorillonite, kind of illite, *et cetera*, and by kind is meant the replacements within the lattice and the character of the exchangeable bases. Replace-

ments are possible within the lattice of some clay minerals, such as iron and magnesium for aluminum in the illites and montmorillonite, and aluminum for silica in the illites and possibly some montmorillonites. Such substitutions almost certainly reflect environmental conditions, but as yet almost nothing is known regarding the conditions controlling possible replacements. This is a very fruitful field for research. It is known that replacements may cause very great changes in properties, even to altering the habit of the clay mineral. Thus, as iron replaces aluminum in the montmorillonite lattice, the mineral changes from flake-shaped to lath-shaped, at least under certain conditions. There are probably other factors that lead to an elongate rather than equidimensional unit, but they are not known.

Researches on Recent sediments are much needed. Considerable data on the origin of clay minerals are coming from soil studies and synthesis experiments, and the compositions of many ancient sediments are fairly well known. Investigations of Recent sediments to fill in the gap are necessary to provide information on diagenetic processes and to permit an evaluation of the sedimentary history of ancient sediments. Such researches must be complete in that the detailed character of *all* the clay minerals in the sediments must be determined. A very small amount of one clay-mineral component may be the key to the evaluation of sedimentary history. Further, the clays must be studied in relation to the factors of the environment, that is, character of water, electrolyte contents, bacteria, and organic content.

## CLAY MINERALS AND ORGANIC COMPOUNDS

Organic material may be present in argillaceous sediments in two ways: first, as discrete particles mechanically mixed with the clay minerals and the non-clay minerals, and second, as molecules adsorbed (3) on the clay-mineral surfaces, mostly the basal-plane cleavage surfaces.

The unit cell of montmorillonite is a sheet-like structure whose flat surfaces are planes of oxygen atoms arranged in a definite pattern (7) (Fig. 1). Of very great significance is the point that the configuration and dimensions of this pattern of oxygen atoms is such that there is a very close possible fit (1) with the configuration and dimensions of the structural arrangement of the carbon atoms in certain organic compounds. Certain clay minerals have a catalytic effect on certain organic compounds, and it has been reasoned that this catalytic effect is a consequence of the approximate fit of the structures of the clay mineral and the organic compounds.

Adsorption of organic compounds is probably due to a combination of structure of the surface, cleanness of the surface, and replacements within the lattice. With regard to cleanness of surface, it appears that the presence of certain cations, and possibly anions adsorbed on the clay-mineral unit surface, will prevent the adsorption of organic materials. Exceedingly small amounts of such ions may have very large detrimental effects. Conversely, there is some slight reason to believe

that certain other ions, again in very small amounts, may have a large beneficial effect. Replacements within the lattice appear to be of great importance—the effect on organic material of one variety of montmorillonite is much greater than that of another. In fact only certain kinds of montmorillonite seem to have the catalytic property to an important degree.

Obviously, from the foregoing, the relation of clay minerals to organic compounds varies with the kind and variety of clay mineral. For example, kaolinite

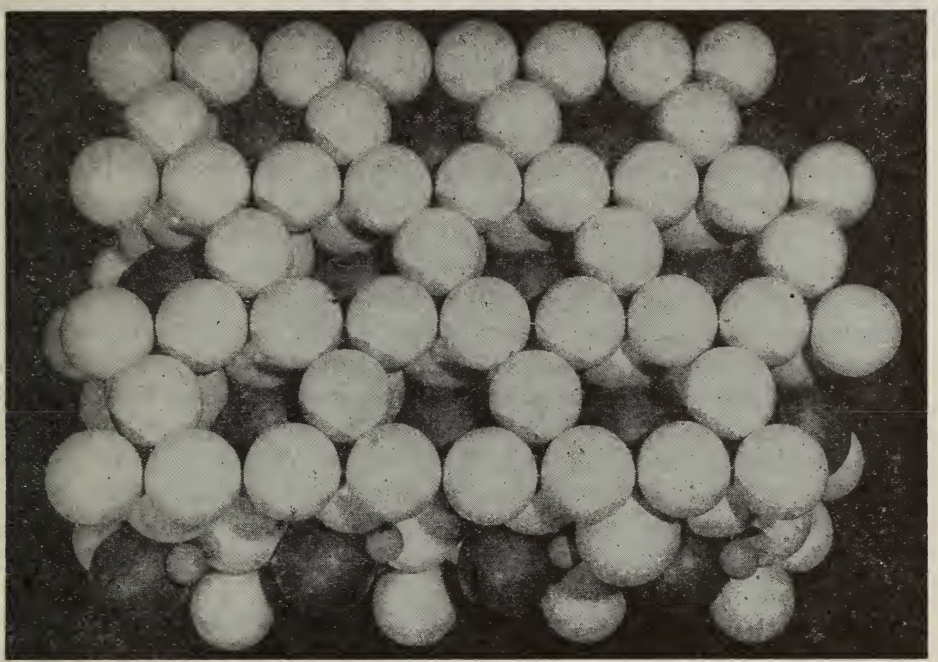

FIG. 1.—Structure of montmorillonite showing, particularly, hexagonal configuration of oxygen atoms (white balls) of basal plane surfaces of unit cells. Black balls represent hydroxyls and small gray balls represent aluminum. Silica atoms are at center of tetrahedron of four oxygens and can not be seen.

would have this property to a slight degree whereas certain varieties of montmorillonite have it to a very high degree.

The significant point is that the clay minerals could well be an important instrument whereby buried organic material is changed to oil. This is an exceedingly fertile field for research, and many specific problems could be mentioned, for example: differences in the catalytic effect of the varieties of the montmorillonite clay minerals; amounts and kind of any organic material adsorbed in Recent argillaceous sediments. The fruits of successful researches in such directions are so obvious that they do not require elaboration; however, one point may be mentioned. There is some reason to believe that if a clay mineral acted as a catalyst in

the transformation of organic material to petroleum, a residue of carbon would be left behind on the catalytic surface. If that were so, we might have a potential clue to determine whether or not a clay mineral has so acted in the past.

### CLAY MINERALOGY AND RECOVERY OF PETROLEUM

Clay minerals are found in sands and sandstones as discrete particles mixed with the quartz grains and as a film plastered around the quartz grains, or only as a film around the grains. In the movement of a fluid through a sand, the objective would be not to disturb the clay-mineral particles in any way that would cause them to occupy the interstices between the sand grains, thereby plugging the sand.

In order to consider the matter in more detail, let us assume a sand containing some small amount of clay composed of montmorillonite. Whether the clay is present in discrete particles or as a film coating the quartz grains, it will be made up of layers of aluminum silicate separated from each other by layers of water from one to several molecules thick (7). Also between the aluminum silicate layers and on their surfaces there will be cations which are exchangeable. The thickness and character of the water between the individual aluminum silicate sheets is largely due to the character of the exchangeable cations which happen to be present. Thus, in an air-dried state, a layer of water a single molecule thick may be present if sodium is the cation, whereas if calcium is the cation the layer of water will be two molecules thick. In the presence of large amounts of water, the water layers for a sodium montmorillonite become indefinitely thick with a thickness depending only on the amount of water present. When calcium is the exchangeable cation the water layer tends to be restricted to a few molecules in thickness regardless of the amount of water available.

The adsorbed cations are exchangeable, that is, if calcium is present on the montmorillonite in the sand, and water containing sodium in certain concentrations moves through the sand, a base-exchange reaction will result in which sodium goes on the montmorillonite in exchange for calcium which leaves the montmorillonite and is carried away by the water. The important thing and the point to be made here is that as a consequence of such an exchange reaction, the relation between the aluminum silicate and the water layer would no longer be stable and a new one would tend to develop. The result of the development of a new equilibrium would probably be the separation of the individual flakes, a splitting of discrete clay particles, and an unplastering of the quartz grains. The net result would be the liberation of minute clay-mineral particles which would plug the sand.

It follows from the foregoing discussion that the presence of sodium in water moving through a sand containing a calcium montmorillonite clay would probably tend to cause clogging, whereas, if the montmorillonite carried sodium as the exchangeable base, there might be little clogging. Similarly for a calcium montmorillonite clay, calcium in the water would probably have little clogging

effect. In water-flooding operations it would seem desirable to know the character of any clay component in the sand and the nature of its exchangeable base.

The situation would be much less critical if some clay mineral other than montmorillonite made up the clay in a sand. Kaolinite for example has low base-exchange capacity and the aluminum silicate layers are held together tightly without intervening water layers (4). As a consequence it has less tendency to break into very small units because of variations in character of the cation. The illite clay minerals are intermediate between kaolinite and montmorillonite in their tendency to break up because of cation variations.

In natural sands one is apt to find a mixture of clay minerals, such as a small amount of montmorillonite interlaminated with illite. The interlamination is apt to be on an exceedingly minute scale, that is unit cells of montmorillonite and illite interlaminated. In such mixtures the montmorillonite provides potential planes of weakness along which the whole particle could break down. Under such conditions a relatively small component of montmorillonite in a clay would cause the whole clay to be sensitive to variations in the character of the cation. In studying such problems it is not adequate to determine only the abundant clay-mineral components—the determination must be complete including those present in only very small amounts.

It is well known that the dispersibility of kaolinite and illite clays in water varies somewhat with the kind and amount of electrolyte. This is a matter of the charge on the clay-mineral particle and not exactly the same phenomenon previously discussed. However, the over-all conclusion would still be the same, namely, that the character of the electrolyte content of the clay and water should be compatible—at least the electrolyte content of the clay should be known.

Another factor in the relation of clay mineralogy to the recovery of petroleum is that some organic compounds can be adsorbed on the surface of the clay minerals—probably to a very limited extent for kaolinite and to a very great extent for montmorillonite, because of the structure of the surface and the potentially great amount of surface per unit weight. Some hydrocarbons in oil sands are probably adsorbed on the surface of the clay-mineral units. Any attempt to sweep off such hydrocarbons would probably also accomplish a separation of the clay-mineral flakes and a clogging of the pores.

An important point in the cation adsorption and base-exchange properties of clay minerals is that there is a high degree of selectivity which varies among the different clay minerals for different cations (11). Not all of the ions are exchanged with equal ease—thus it is easier to exchange calcium for sodium on a clay mineral than it is to replace the calcium held on a clay by sodium. Further the relative ease of the exchangeability of two cations is not the same for all the clay minerals. This selectivity probably should be the point of departure for researches to devise methods and materials to better control the dispersibility of the clay component of sands. It can be pointed out that very small amounts of certain materials, for example, the complex phosphates, greatly influence the

development of the adsorbed water, at least in certain clay minerals. There is a possibility that certain chemicals may be found which will inhibit the development of adsorbed water which causes dispersion of the clay particles.

Researches are in progress in the laboratory of the Illinois State Geological Survey on the character of the clay mineral in the producing formations in Illinois. The character of the clay mineral varies in different sands, and although it is too early to state conclusions, the results appear to have promising value in planning water-flooding operations.

### CLAY MINERALOGY AND DRILLING MUDS

The relation of clay mineralogy to drilling muds is a big subject and perhaps beyond the field of interest to many in this group. It is proposed here to make only a few points which illustrate certain attributes of the clay minerals that are demonstrated in drilling muds and that are of general importance to the problems at hand.

A characteristic of the montmorillonite clay minerals is that water enters between the unit cells which are about 9.5Å thick, and that layers of water develop between the units, thereby separating them (7). In montmorillonites of certain kinds and when sodium is the exchangeable base, water layers of great thickness may be formed, in fact the thickness is dependent on the amount of water, and the individual units may be substantially completely separated from each other. In such montmorillonites, and probably in other clay minerals as well, the water layers between the units are made up of oriented water molecules (12), that is, there is a definite pattern or structure to the water—it is crystalline. The orientation of the water molecules begins at the surface of the montmorillonite unit because of the structure of the oxygen atoms in the surface layer, and continues outward from the surface through large distances in such montmorillonite. A certain amount of time, usually measured in minutes, is required for the orientation to be completed. The orientation is not very rigid and can be destroyed by agitation. The orientation accompanied by the development of rigidity develops again after agitation ceases. This is the property of thixotropy so important in drilling muds.

In other kinds of montmorillonite and in those with some exchangeable bases other than sodium, water seems to enter between the individual layers only to a very limited extent, so that even though the water itself is composed of oriented water molecules, the property of thixotropy is substantially absent.

Of considerable general importance is the fact that small amounts of certain cations and anions exert a large influence on the perfection of the orientation of the water, the thickness to which it develops, and the rate of the development of the orientation. Certain complex phosphates, for example, in exceedingly small amounts may greatly alter the properties of a drilling mud. This illustrates a very significant generality regarding clays, namely, that certain materials in very small amounts very greatly influence the properties of certain clays. The explanation

for the effect of the phosphates probably rests in the approximate structural fit of the phosphate in the water lattice thereby distorting but not destroying entirely the oriented water.

Clay mineralogy is important also in the refining of petroleum—in the preparation of decolorizing agents and catalysts. This matter is probably beyond the field of petroleum geology. However, it should not be overlooked in any broad research investigation of clay mineralogy in the petroleum industry, not only because of its immediate economic importance to refining, but also because of the light it might throw on the possible catalytic action of clay minerals on the organic material in sediments.

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